United States Patent

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[33] Italy
[31] 746551/65
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[54] GETTER DEVICE
10 Claims, 3 Drawing Figs.

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[51] Int. Cl. F04b 37/02, B23p 3/00, H01j 7/18
[50] Field of Search 29/191.2, 192, 195, 183.5, 420; 417/48, 49, 51; 252/181.6; 316/25; 313/7, 174; 315/108, 111; 324/33; 250/84.5

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ABSTRACT: A getter device comprising a carrier having on at least one of its faces particles of a nonvaporative getter metal characterized in that the particles of the getter metal are partially embedded in the carrier to give a highly efficient getter device.

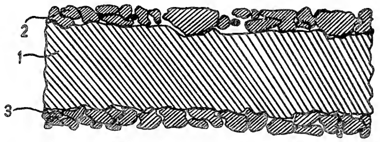


Fig.1

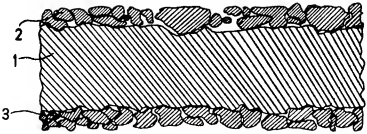


Fig.2

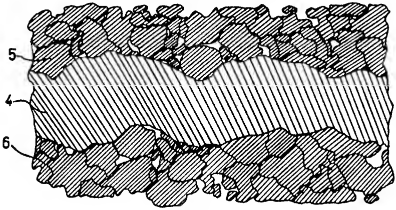
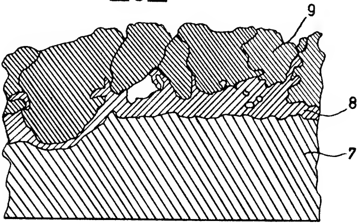


Fig.3



GETTER DEVICE

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation of U.S. application, Ser. No. 527,906 filed Feb. 16, 1966, now abandoned.

This invention relates to getter devices formed by a carrier, at least one of whose faces carries a thin layer of particles of a hard nonvaporative getter metal. Such getter devices are employed in closed vessels such as electronic tubes to create and/or maintain vacuum.

In the getter art there is a longfelt need for a getter device having a large free surface of nonvaporative getter metal. Such a getter device must have a high mechanical strength and satisfactory thermal properties.

It is known that in the manufacture of getter devices employing nonvaporative or "bulk type" getter metals according to prior methods, certain defects are experienced. These involve, in the case of the bulk getters the necessity of exerting a special care in order that adequately large areas of active surface of the getter metal are obtained by employing economically acceptable amounts of getter metal.

The prior methods for the manufacture of nonvaporative getter devices can be divided into the following two categories:

1. Tabletting a powdered getter metal; and
2. Securing powdered getter metals to the surface of a carrier by means of chemical binders, and subsequent sintering.

Actual examples of manufacture of getter devices with methods of the first class are:

a. Cold-pressed tabloids enclosed in perforated cladding material. In order that adequate mechanical and thermal properties may be obtained for the tabloids, it is necessary in this instance to compress the powder under rather high pressures, with a resultant decrease of the porosity and thus of the active specific surface. Moreover, since no intimate heat-transfer contact can exist between the tabloid and its cladding material, the activation of these getter metals by heating is toilsome.

b. Cold-compressed powders or tabloids admixed with a chemical binder by pressure onto suitably shaped carriers so as to have at least one face of active getter metal exposed to the gases to be absorbed. The method for obtaining this kind of getter device requires pressures which are lower than those necessary for the former method (a), a satisfactory mechanical stability being obtained, along with a fair heat-transfer contact, owing to the intimate contact between the getter metal and the carrier. At any rate, in order that satisfactory mechanical and thermal properties may be achieved, it is necessary, similarly to what occurred with the former case (a), to employ a considerable amounts of powdered getter metal only 10 percent (approx.) of which is active, whereas the remaining 90 percent has the only task of forming a sufficient bulk of compacted powder, so as to retain the same within the container.

Such getter devices employ chemical binders to attach the getter metal to the carrier greatly jeopardizing the gas-sorption quality of these getter devices. As a matter of fact, it is not possible to completely remove the binder upon the sintering step. As the temperature is increased, the binder is dissociated into gaseous components and solid residues. A major portion of the gaseous components is absorbed by the getter metal and thus a considerable fraction thereof is already exhausted prior to its practical proper use. Solid residues, when made up of silicates, melt and mask a considerable fractional area of the getter device. The binder residues are of a carbonaceous nature, undesirable hydrocarbons can be formed within the electronic tube, or the like, in which the getter device is to be used.

c. Extremely fine powder (the grain size is in the order of magnitude of 1 micron), compressed in the cold and milled thereafter to a coarser grain size (200–500 microns), said coarser grains being within a container formed, wholly or partially, by a very fine-mesh wire gauze (100 microns). The defects exhibited by these getter devices are very much the same as those of the getter devices in the case (a) above, while the mechanical properties are still worse. There is, however, the advantage of an almost total utilization of the employed powder for gas-sorption. Nonetheless, the method for preparing such getter devices is rather intricate and costly and has no practical industrial application because of the high cost of the resultant device.

None of the above enumerated manufacturing methods, the only exception being the case (c) which has no industrial application, is capable of giving geometrical surfaces for the getter devices in excess of 2 to 3 square centimeters, while the truly active surface could be about 10 times the geometrical surface. At any rate, however, the specific active surface area does not exceed about 0.07 square centimeters per milligram.

A specific object of the present invention is therefore to provide a getter device having considerable advantages over prior devices as obtained with the prior art methods. More particularly, another object of this invention is to provide a getter device employing bulk getter metals having a greater ratio of active surface area to mass of the getter metal used, with a considerable economy in the use of getter metals, a high purity of the same, and all this in combination with a high mechanical robustness and valuable thermal characteristics.

According to the present invention there is provided a getter device which comprises a carrier having a thin layer of powdered getter metal characterized in that the carrier material is softer than the powdered getter metal the particles of which are partially embedded in the carrier.

The getter devices of the present invention are produced by a process which comprises the step of anchoring the particles of the powdered getter metal to the carrier's surface, said carrier being composed of a material softer than the powdered metal. The anchoring is accomplished by a localized pressure applied at room temperature, so as to cause the particles to be partially embedded in the carrier material and to produce cold microwelds between the particles and the surface of the carrier.

The invention, moreover, exploits the fact that it is possible to apply, to a thin layer of metallic getter particles, a pressure which causes them to be mutually welded preferably along the direction of the applied force rather than in any other direction whatsoever. It becomes thus possible to reduce both the number and the strength of the welds in a direction which is parallel to the carrier surface.

In addition, it has been found that such a phenomenon can take place whenever the thickness of the metal particles layer does not exceed certain limiting values. More precisely, it has been ascertained that such a layer, when metal particles having an average grain size of about 50 microns, are used, should not exceed the thickness of about 250 microns.

The invention will now be described in more detail, reference being had to the accompanying drawing in which a few exemplary configurations of getter devices of the present invention are schematically illustrated on an enlarged scale.

In the drawings:

FIGS. 1 and 2 are cross-sectional illustrations, with an enlargement of about 300 diameters, of two getter devices obtained according to an embodiment of the present invention and

FIG. 3 is another example of a getter device also shown in cross-sectional view, the enlargement being of about 1,300 diameters.

According to a first embodiment of the present invention a single and even layer, whose thickness is of the same order of magnitude as the average diameter of the particles of the getter metal, is spread over the surface of a material which is softer than the getter metal, a strongly localized pressure being applied to the particles along a direction which is virtually perpendicular to the surface of the carrier material, so as to cause the particles to become partially embedded in the carrier surface.

According to another embodiment of the present invention an even layer having a thickness which is a multiple, such as four or five times the average diameter of the particles forming the active getter metal is spread over a face of the carrier material, a localized pressure being applied, as outlined above, on the layer of active getter metal, said pressure being sufficient to produce local welds (predominantly in a direction orthogonal to the carrier surface), among the particles which are not in direct contact with the surface of the carrier, whereas the particles contacting said surface are also in this case, partially embedded in the carrier surface, partially welded thereto on a microscopical scale.

According to a further embodiment of this invention, the active getter metal is embedded into both faces of the carrier, thus producing a getter device having dual-active surfaces. The geometrical dimensions are limited only by the specific intended use of the getter device.

Having now particular reference to the accompanying drawing and initially to FIG. 1 thereof, showing a stainless steel carrier 1, having on both faces thereof layers of powdered zirconium alloy 2 and 3, whose average thickness is equal to the average diameter of the particles.

FIG. 2 shows, on each face of an iron carrier 4, a layer of powdered zirconium alloy, 5 and 6, whose average thickness is three times the average diameter of the particles.

The carrier can be the entire substrate or can comprise a coating on another substrate as long as the hereindescribed hardness relationships are maintained.

The localized pressure on the active material particles which had been previously deposited in a uniform manner on the carrier, can be applied with a number of suitable means. Typical of mechanical means capable of inducing the required pressure are conventional rolling mills or hydraulic presses. It is also possible to exploit the known pressure effect afforded by extremely intensive, instantaneously applied magnetic fields, or, as an alternative, to bombard the soft carrier surface with the harder particles by means of gas jets at high velocities and pressures and by plasma jets.

The preferred method is the compression of the particles against the carrier material by means of a body which is interposed between the particles and the compressing members, said intermediate body being comparatively hard with respect to said carrier material and acting as a deformable padding or cushion. This intermediate body should be endowed with the property of being readily liable to work-hardening by deformation in the cold state, so as to withstand an excessive penetration therewithin of particles having a size over the average, while reaching, however, with its surface which has not yet been engaged by the points of the surrounding tiny particles, the points of the latter so as to exert on them also an adequate compressive action. The result of this is that virtually all of the particles are effectively and individually compressed onto, and embedded into, the carrier material, the adherence of the whole assembly being perfect and the exposed rugged surface of getter device being still larger than that obtained by compression with very hard materials, such as hardened steel or metal carbides which are harder than the getter metal.

Examples of intermediate bodies having outstanding characteristics are plain carbon steel or Fe-Ni-Cr alloys and a number of stainless steels. Said intermediate bodies can then be readily separated from the final products.

By way of example, acceptable values of hardness of the various materials used for obtaining a metallic body according to the invention can be indicated as follows:

	Vickers hardness
Carrier material	90 kgs./sq. mm.
Powdered getter metal	400 kgs./sq. mm.
Material of the intermediate body	180 kgs./sq. mm.
Compressive force	500 kgs./sq. mm.

Referring now to FIG. 3 there is shown an iron carrier 7, a plated layer of aluminum 8 and, thereover, a layer of a powdered zirconium alloy 9 whose average thickness is equal to the particle average diameter.

According to a still further embodiment of the invention, the carrier formed by a suitable plating material and having the active getter metal embedded therein, can be directly welded to the surface of an internal member of an electronic tube.

A few examples of materials which can be used according to the invention for acting as a carrier for getter metals are as follows: iron, nickel, aluminum and stainless steel. Appropriate plating materials are, for example, aluminum, nickel, titanium and chromium. Examples of plated substrates include among others aluminum-clad iron, and aluminum-clad iron-nickel.

Examples of suitable nonvaporative getter metals capable of reacting with gases include among others titanium, zirconium, thorium, vanadium, tantalum, niobium, tungsten, and alloys of two or more thereof. These getter metals can also be alloyed with other metals such as aluminum, cerium, manganese, sodium, or "Mischmetall" (for example a mixture of cerium and lanthanum) so as to afford a selective gas-sorptive action, or a more complete absorption, or also a high efficiency within wide temperature ranges. The powders used as active getter metals can also comprise mixtures of different powdered getter metals. Nonvaporative getter metals comprise a class of materials well known in the getter art as shown for example by U.S. Pat. No. 2,926,981 to Stout et al. and U.S. application Ser. No. 173,503 filed Feb. 15, 1962, now U.S. Pat. No. 3,203,901. The use of nonvaporative getter metals in getter devices is illustrated in numerous U.S. and foreign patents such as U.S. Pat. Nos. 3,195,716 and 3,225,910.

Although barium or barium containing alloys can be employed in combination with the getter devices of the present invention they are unsuitable for use as the sole getter metal because (1) they are vaporative rather than nonvaporative getter metals and (2) they are softer rather than harder than the preferred metallic carriers employed in the present invention.

The invention can be applied to the production of getter devices of any desired geometrical shape such as rings, strips, rectangular and square sheets, cylinders or cones. The strips can be folded many times so as to achieve a highly compact structure. Furthermore, the getter devices can be an integral part of the electrodes of any electronic-discharge device, or of an electrode carrier, or they can be a part of a getter device of conventional design.

In a getter device prepared according to the invention by applying to the carrier surface a layer of getter metal particles whose thickness is about five times the average diameter of said particles (for example a layer about 250 microns thick), up to 90 percent of the total surface area of the particles is exposed to the gases to be absorbed. If the getter device upon whose carrier a layer having a thickness equal to the average diameter of the active getter particles is applied, the area of the surface exposed to the gases is about 60 percent of the total particle area. In any case, according to the invention, specific active areas of about 2 (or more) square centimeters per milligram can be obtained.

Getter devices of the present invention exhibit mechanical and thermal characteristics which, both before and after the high-temperature activation, approach to a degree those of the carrier materials. It has been seen, in practice that these getter devices easily withstand mechanical shocks induced, for example, by ultrasonic treatments and thermal stresses induced by a quick heating up to 1,000° C. or over. A further advantage afforded by the getter devices of the present invention, lies in that they neither require binders nor dispersants for the initial formation of the thin layer of getter metal particles on the carrier material and consequently the defects inherent in the use of binders or other agents are wholly avoided.

The whole process of manufacture of getter devices of the present invention can be carried out under conditions of extremely high purity and is unaffected by the pollution caused

by manual handling, since such a handling in unnecessary. As a matter of fact, it is not necessary that the getter devices be exposed to inert-gas surroundings prior to their actual use. Thus, the starting materials used in the production of these getter devices can be degassed and treated as specified and then directly passed to the production machine which does not necessitate or require the use of oils or lubricants, the final getter devices being directly dropped in containers which are sealed immediately thereafter. All the manufacturing stages of the getter devices can be performed with the greatest ease by automatized methods and within a protective inert atmosphere. An important feature of the getter devices of the present invention in the nonplanar upper surface of the particulate getter metal attached to the carrier. This nonplanar surface is caused by the use of an intermediate body as described above and is important to the gas-sorptive capacity of the getter device. Getter devices having planar upper surfaces produced by processes such as simply rolling particulate getter metal on a carrier or substrate have a greatly reduced sorptive capacity.

The getter devices obtained according to the invention can be used wherever it is desired to produce a high vacuum or wherever the gas contents of an enclosure should be kept under control. Thus, the getter devices can be used in the manufacture of several types of bulbs, electronic-discharge devices, gas-filled tubes, mercury-filled tubes, transistor containers and the like, and in getter pumps and ion-pumps as well.

What is claimed is:

1. A getter device comprising a carrier having in correspondence with at least one of its faces, a thin layer of particles of a hard, nonvaporative getter metal characterized in that the carrier material is softer than the getter metal whose particles are partially embedded in the carrier material.

2. The getter device of claim 1 wherein the particles form a layer, the upper surface of which is nonplanar.

3. A getter device which when heated in a vacuum sorbs gases said device comprising:

A. a carrier,

B. a layer of finely divided particles of a nonvaporative getter material partially embedded in at least one surface of said carrier and cold welded to at least one surface of said carrier.

4. A getter device which when heated in a vacuum sorbs gases, said device comprising:

A. a metallic carrier,

B. a layer of finely divided particles of a nonvaporative getter metal which are harder than said metallic carrier and are partially embedded in at least one surface of said carrier and cold welded to at least one surface of said carrier.

5. A getter device which when heated in a vacuum sorbs gases, said device comprising:

A. a metallic carrier,

B. a layer of finely divided particles of a nonvaporative getter metal which are harder than said metallic carrier and are partially embedded in at least one surface of said carrier and cold welded to at least one surface of said carrier, and wherein said layer has a nonplanar upper surface.

6. A getter device comprising:

A. a metallic carrier,

B. a layer of finely divided particles of a nonvaporative getter metal selected from the group consisting of zirconium, titanium, thorium, vanadium, tantalum, niobium, tungsten, mixtures thereof and alloys thereof with one another or with aluminum.

7. The getter device of claim 6 wherein the nonvaporative getter metal is a zirconium-aluminum alloy.

8. A getter device comprising:

A. a stainless steel carrier,

B. particles of a zirconium getter alloy embedded in the carrier.

9. A getter device comprising:

A. a metallic carrier,

B. an even layer of particles of a nonvaporative getter metal on the carrier, the layer having a thickness of about four times the average diameter of the particles, the particles being held together by local welds predominantly in a direction orthogonal to the surface of the carrier, the particles contacting the surface of the carrier being partially embedded therein.

10. A getter device comprising:

A. a metallic carrier,

B. an even layer of particles of a nonvaporative getter metal on the carrier, the layers having a thickness of about four times the average diameter of the particles, the particles being held together by local welds predominantly in a direction orthogonal to the surface of the carrier, the particles contacting the surface of the carrier being partially embedded therein, the ratio of surface area of getter metal to weight of getter metal exceeding about 2 $cm.^2/mg$.

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